

O₂ Diffusion in SiO₂: Triplet versus Singlet

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We address the diffusion of the oxygen molecule in SiO₂, using first-principles spin-polarized total-energy calculations. We find that the potential energy surfaces for the singlet and triplet states are very different in certain regions, and that the O₂ molecule preserves its spin-triplet ground state not only at its most stable interstitial position inside the solid but also throughout its diffusion pathway. Therefore, the singlet state is not a good approximation to describe the behavior of O₂ inside SiO₂, and spin-polarization effects are fundamental to understand the properties of this system.

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Silicon oxide and oxynitrides are key materials for silicon-based microelectronic devices. They are used as gate dielectrics in metal-oxide-semiconductor field-effect transistor and dynamic random-access memory devices [1]. As the number of devices per chip continues to increase, coupled with the obvious scaling down of all components, the atomistic understanding of all processes involved in silicon oxidation becomes crucial. Thermal oxidation of Si in a dry O₂ atmosphere is the method of choice to grow silicon oxide films on top of Si substrates (even for oxynitrides, it is important to understand the growth of pure SiO₂, since the nitridation may be performed on preoxides) [2].

Interstitial oxygen plays an important role in the thermal oxidation process, either through the interaction with point defects, or, as many results indicate, as the promoter of the oxide growth after diffusing through the silica network [2]. In the widely established Deal-Grove model [3], which works well for films thicker than approximately 100 Å, SiO₂ grows via O₂ diffusion through the oxide, reacting with silicon at the Si/SiO₂ interface. For ultrathin silicon oxide films (<50 Å), however, the oxide growth mechanism does not follow the Deal-Grove model [4], and there might be alternative diffusion mechanisms for oxygen in silicon oxide which might involve the dissociation of O₂ molecules. In fact, recent theoretical studies have considered diffusion processes involving atomic oxygen in the peroxy configuration [5–7]. In any case, the requirement for increasingly thin insulating oxide layers highlights the importance of an accurate, atomic-scale understanding of the properties of interstitial oxygen molecules in SiO₂, as well as a description of the O₂ diffusion mechanism in it.

As is well known, the ground state of the oxygen molecule in the gas phase is the triplet $^3\Sigma_g^-$ state, with the two lowest-energy excited states being the singlets $^1\Delta_g$ (excitation energy of 0.98 eV) and $^1\Sigma_g^+$ (excitation energy of 1.63 eV) [8]. It has been shown that during the oxidation of the Si(100) surface there is a triplet-to-singlet conversion [9], which is crucial in explaining the dependence of the sticking probability as a function of the incident energy. There is some experimental as well as theoretical

evidence that the interstitial O₂ in SiO₂ also has a triplet ground state [7,10]. Hence, one may ask the question if there is also a triplet-to-singlet conversion inside the SiO₂ related to any process that involves the oxygen molecule. In particular, during the hopping between two interstitial sites, it is expected that there is a stronger interaction of the O₂ molecule with the lattice. Therefore, it might happen that there is a triplet-to-singlet conversion during the diffusion of oxygen molecules. In this paper we address this question. We show, using α quartz as a model for the SiO₂ network [5–7], that (i) the interstitial O₂ molecule ground state is a triplet; (ii) indeed the singlet state is stabilized at the saddle point for the hopping between two interstitial sites; (iii) but the triplet is always the lowest-energy state, and therefore there is not triplet-to-singlet conversion. However, the singlet state is stabilized in such a way that there is a local minimum in the singlet potential energy surface (PES), where there is a maximum for the triplet PES. Therefore, the correct treatment of spin is crucial in the study of the diffusion and most likely other processes that involve O₂ in SiO₂, and the singlet PES cannot be used to properly understand them, contrary to what has been assumed by some authors [5,6].

Our theoretical approach is performed in the framework of the density functional theory [11] and norm-conserving *ab initio* pseudopotentials [12]. The Kohn-Sham wave functions are expanded using a plane-wave basis set [13], with an energy cutoff of 64 Ry. For the exchange-correlation potential we adopt the generalized gradient approximation as proposed by Perdew *et al.* [14], with spin-polarization effects included [15]. As mentioned above, SiO₂ is modeled by the α -quartz structure. We use a 72-atom supercell and the Γ point for the Brillouin zone sampling. The positions of all the atoms in the supercell, plus the O₂ molecule, were relaxed until all the force components were smaller than 0.05 eV/Å.

The calculated structural and elastic properties for the α quartz and gas phase O₂ molecule ($^3\Sigma_g^-$) are compared with the experimental data in Table I. Our structural parameters of α quartz are in good agreement with the experimental results within an accuracy of about 1%. Its

TABLE I. Calculated frequency ν , bond length b , and binding energy E_b for the free O₂ molecule. Equilibrium lattice constants a and c , Si—O bond lengths d , and Si—O—Si bond angle θ for α quartz. Experimental values are included for comparison.

Structure	Parameter	Our results	Experiment
O ₂	ν (cm ⁻¹)	1548	1556.2 ^a
	b (Å)	1.248	1.2074 ^a
	E_b (eV)	6.488	5.213 ^a
α quartz	a (Å)	4.966	4.92 ^b
	c (Å)	5.472	5.41 ^b
	$d_{\text{Si-O}_1}$ (Å)	1.625	1.605 ^b
	$d_{\text{Si-O}_2}$ (Å)	1.628	1.614 ^b
	$\theta_{\text{Si-O-Si}}$ (deg)	143.8	143.7 ^b

^aReference [17].

^bReference [18].

calculated band structure gives an indirect gap of 5.85 eV, between the valence band maximum (VBM) at the M point and conduction band minimum (CBM) at the Γ point. Our results for the O₂ vibrational frequency and its equilibrium bond length are within an accuracy of 0.5% and 3%, respectively. The binding energy shows a larger deviation ($\sim 20\%$), which is usual for this molecule at our level of approximation [16].

To determine the lowest-energy configuration for an interstitial O₂, we positioned the molecule inside the largest interstitial site of α quartz, in three mutually perpendicular orientations, and then allowed the whole system to relax. This procedure was done for the triplet and singlet states. In the lowest-energy structure, for both spin states, the O₂ is oriented along the (100) direction normal to the c axis, as shown in Fig. 1(a). Both the triplet and singlet final geometries are very similar, and in Fig. 1(a) we actually present only the triplet configuration, which is 0.9 eV lower in energy than the singlet configuration. The O₂ bond length in the triplet state is 1.245 Å, similar to the

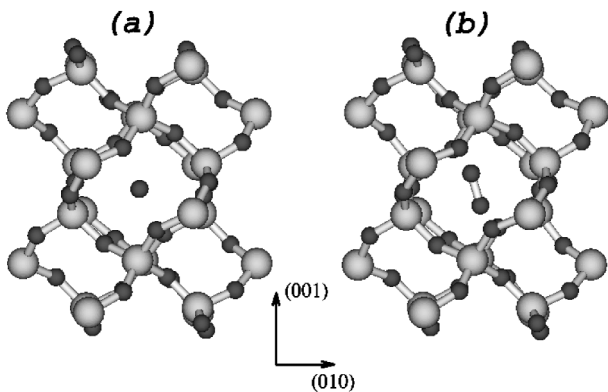


FIG. 1. Equilibrium configurations of the interstitial O₂ molecule in α quartz in the spin-triplet state. (a) Minimum-energy structure. (b) Metastable structure. The small circles represent oxygen atoms and the larger circles represent silicon atoms.

gas phase value. The formation energy for the inclusion of O₂ in α quartz is found to be 2.7 eV, in fair agreement with other recent theoretical calculations [7]. In Fig. 1(b) we show our final configuration with the O₂ oriented approximately along the c axis. This configuration has been considered by some authors [5,6] as the ground state configuration. However, for the triplet state, we find it to be 0.1 eV higher in energy than the configuration shown in Fig. 1(a), whereas, for the singlet state, it is 0.2 eV higher in energy (again, the final geometries are very similar for both spin states).

A possible diffusion pathway was considered along the (100) direction, through a line that joins two neighboring interstitial configurations of the type shown in Fig. 1(a) (called I_a from now on). Along this line, we considered three additional interstitial positions: one midway between two I_a 's (called I_d from now on), and the other two distributed evenly between the I_a and I_d interstitials (which will be called I_b and I_c from now on). From symmetry it is enough to consider only half of the pathway from two I_a 's (see Fig. 2). The equilibrium structures for O₂ at the additional interstitial sites were obtained constraining the movement of the molecule to a plane normal to the diffusion direction. All the other degrees of freedom were completely relaxed. The final geometries are shown in Fig. 2, and the total-energy profiles through this diffusion pathway, for both the singlet and triplet spin states, are displayed in Fig. 3. We observe that (i) along the diffusion pathway considered, the spin-triplet structure always exhibits the lowest total energy, suggesting that the oxygen molecule preserves its ground state configuration while diffusing in SiO₂; (ii) the PES for O₂ diffusion shows a different behavior according to the spin state. For the spin triplet, we find that the I_a is a global minimum, and the I_d is the top of a rather flat barrier. On the other hand, for the spin singlet, we observe two minima with similar energies at I_a and I_d , separated by a barrier with maximum at I_c . For both triplet and singlet states we find an activation energy for migration of approximately 0.6 eV. However, because of the differences in PES, we expect the singlet and triplet diffusion coefficients to be very different, due to different preexponentials. The measured value for the average activation energy for O₂ diffusion in silica is about 1.2 eV [19], with a significant spread. Our value of 0.6 eV is about half this value, and we believe that the main reason for this discrepancy is the fact that the barrier in the amorphous is significantly higher than in the crystalline phase, as shown recently in Ref. [20].

In Table II, we report results for geometrical parameters at the different interstitial positions. We observe that the average distances between the molecular oxygens and their four SiO₂ nearest-neighbor atoms, which always correspond to O atoms, are approximately the same along the diffusion pathway, being somewhere between 2.4–2.6 Å. The presence of the O₂ molecule perturbs the nearest-neighbor O atoms in α quartz, which tend to relax

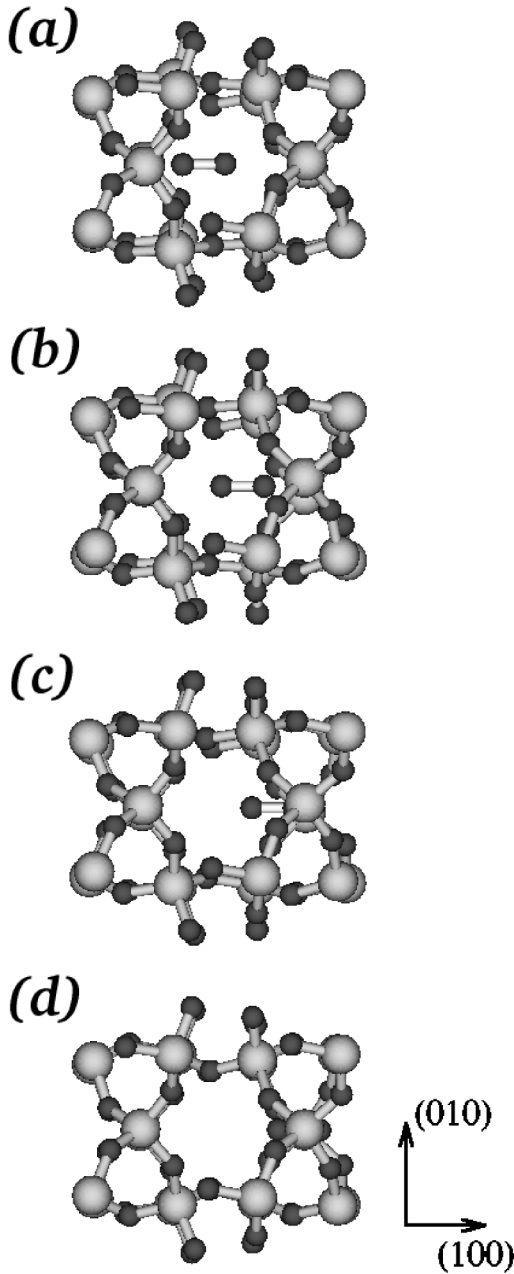


FIG. 2. Local geometry of the O_2 diffusion in α quartz through the (100) direction. (a), (b), (c), and (d) are, respectively, the I_a , I_b , I_c , and I_d O_2 interstitial positions under study.

outward, suggesting a repulsive interaction. The change in lattice energy, E_l , due to the introduction of the O_2 molecule [21], for the spin-triplet state, varies between 0.9 and 1.2 eV. Similar values are found for the spin-singlet state. This indicates that the lattice contribution to the change in the singlet-triplet energy difference, $E_S - E_T$, is negligible.

In order to understand this difference in behavior between the singlet and triplet states, we present in Fig. 4 the Kohn-Sham defect energy levels in the gap, for the triplet I_a and I_d interstitials. In the spin unpolarized free mole-

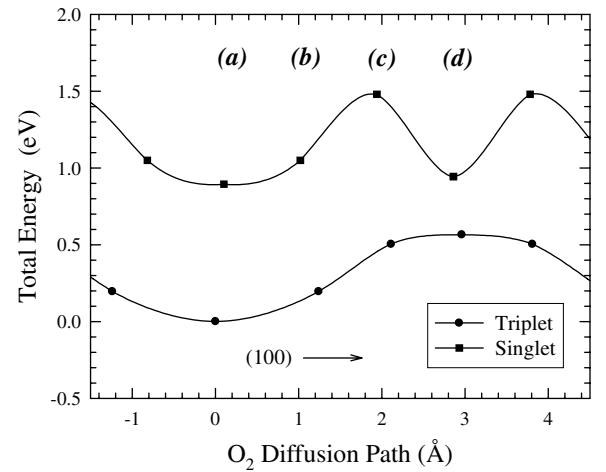


FIG. 3. Energy profile of O_2 diffusion in α quartz through the (100) direction, for both singlet and triplet spin states. (a), (b), (c), and (d) indicate, respectively, the I_a , I_b , I_c , and I_d O_2 interstitial positions in the lattice.

cule, the highest occupied orbitals are the fourfold degenerate $pp\pi^*$ ($\pi_{x\sigma}^*$, $\pi_{y\sigma}^*$; $\sigma = \uparrow, \downarrow$). When spin polarization is considered, there is a splitting between the spin-down and spin-up orbitals ($\varepsilon_{\downarrow} - \varepsilon_{\uparrow}$), and the O_2 molecule has a spin-triplet ground state. This orbital splitting is expected to be proportional to the exchange integral J , i.e., $\varepsilon_{\downarrow} - \varepsilon_{\uparrow} = \lambda J$, where $J = \int \pi_x^*(\mathbf{r}_1)\pi_y^*(\mathbf{r}_2)v(\mathbf{r}_1, \mathbf{r}_2)\pi_y^*(\mathbf{r}_1)\pi_x^*(\mathbf{r}_2)d\mathbf{r}_1d\mathbf{r}_2$, and $v(\mathbf{r}_1, \mathbf{r}_2)$ is the screened Coulomb interaction between two electrons [22] (λ is simply a proportionality factor, to be determined by the calculated values of $\varepsilon_{\downarrow} - \varepsilon_{\uparrow}$ and $E_S - E_T$ for the free molecule). Moreover, it can be shown that the total-energy difference between the singlet and triplet states, for the free O_2 , can be written as $E_S - E_T = \frac{8}{3}J$ [22] (we considered that the singlet energy E_S is a weighted average between the energies of the ${}^1\Delta_g$ and ${}^1\Sigma_g^+$ singlet states). For the free molecule we calculate $E_S - E_T = 1.08$ eV, and $\varepsilon_{\downarrow} - \varepsilon_{\uparrow} = 2.44$ eV. From these values we find that $J^{\text{free}} = 0.41$ eV, in good agreement with the literature [22], and that $\lambda = 6.0$. Inside the crystal, besides the exchange splitting, there is also a crystal-field splitting, Δ_{CF} , between the π_x^* and π_y^* levels. In this case, the total-energy

TABLE II. Geometrical parameters at I_a , I_b , I_c , and I_d interstitial positions, for the spin-triplet calculation. d_{O-O} is the O_2 bond length. $d_{O_{1,2}-NN}$ is the average distance between a molecular oxygen and its four SiO_2 nearest-neighbor atoms, which always correspond to O atoms. E_l is the lattice energy change due to introduction of the O_2 molecule.

Position	d_{O-O} (Å)	d_{O_1-NN} (Å)	d_{O_2-NN} (Å)	E_l (eV)
I_a	1.245	2.43	2.53	0.9
I_b	1.256	2.57	2.54	1.2
I_c	1.256	2.47	2.46	1.0
I_d	1.262	2.49	2.45	1.0

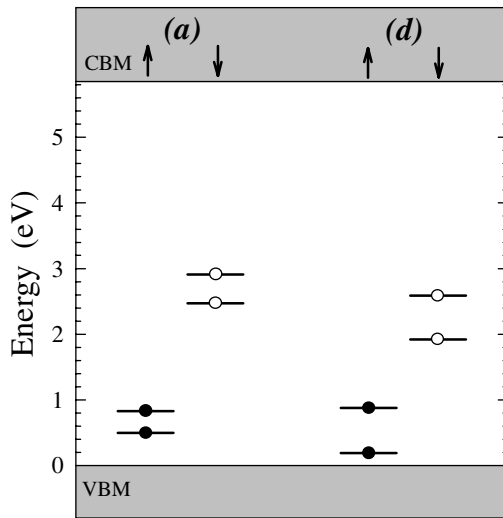


FIG. 4. Schematic representation of the Kohn-Sham energy levels in the band gap of α quartz, for the interstitial positions I_a and I_d , in the triplet configuration. Filled and open dots indicate occupied and empty states, respectively. The arrows indicate spin-up and spin-down energy levels.

difference $E_S - E_T$ becomes $E_S - E_T = \frac{8}{3}J - \Delta_{CF}$ (the crystal-field splitting stabilizes the singlet with respect to the triplet state). For I_a we have $E_S - E_T = 0.9$ eV, $\varepsilon_l - \varepsilon_t = 2.0$ eV, and $\Delta_{CF} = 0.3$, and, for I_d , $E_S - E_T = 0.4$ eV, $\varepsilon_l - \varepsilon_t = 1.9$ eV, and $\Delta_{CF} = 0.7$. Therefore, there is a change (δ_{ad}) in the $E_S - E_T$ of 0.5 eV between I_a and I_d , i.e., $\delta_{ad}(E_S - E_T) = 0.5$ eV. Assuming that λ does not change, we have $J^a = 0.33$ eV, and $J^d = 0.32$ eV. These values for the exchange integrals give $\delta_{ad}^J(E_S - E_T) = 0.1$ eV. Hence, the small reduction in the exchange integral between I_a and I_d does not suffice to explain why $\delta_{ad}(E_S - E_T) = 0.5$ eV. However, there is a change in the crystal-field splitting between I_a and I_d of $\delta_{ad}(\Delta_{CF}) = 0.4$ eV, which gives a contribution to the change in $E_S - E_T$ between I_a and I_d of $\delta_{ad}^{\Delta_{CF}}(E_S - E_T) = 0.4$ eV. This value, when added to the exchange contribution, gives the correct result of $\delta_{ad}(E_S - E_T) = 0.5$ eV. In summary, the singlet-triplet splitting is approximately equal to 0.9 eV at the I_a , I_b , and I_c interstitial positions, but is reduced to 0.4 eV at I_d . This reduction of 0.5 eV is mostly ($\sim 80\%$) due to an increase in the value of the crystal-field splitting, but also has a contribution of $\sim 20\%$ due to a reduction in the value of the exchange integral J .

In conclusion, we find that (i) the ground state of interstitial O_2 in α quartz is a spin-triplet state; (ii) O_2 largely preserves its molecular character inside the crystal. This is supported by charge-density plots, which indicate that,

for all the interstitial sites considered, the O_2 gap levels correspond to the π_x^* and π_y^* molecular orbitals; (iii) the triplet and singlet PESs for O_2 diffusion in α quartz are very different. This indicates that the correct treatment of the spin degree of freedom is crucial in studies of O_2 diffusion in SiO_2 .

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